

## DECOMPOSITION OF FERRICENIUM CATION IN ALKALINE MEDIUM

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Stoichiometry and kinetics of decomposition of ferricenium compounds have been studied in alkaline medium. The reaction stoichiometry depends on type of the ferricenium compound. The decomposition rate of ferricenium ions is affected significantly by the presence of anions of inorganic salts with which ferricenium ion forms relatively stable complexes. From time course of the reaction probable mechanism of the decomposition process has been suggested, and its kinetic parameters have been determined.

Ferricenium ion and its substitution derivatives are slightly stable in alkaline media being decomposed through a rather complex redox process giving ferrocene or its derivative, respectively. The available literature data concerning this reaction are considerably contradictory. Differences in experimental stoichiometric ratios of the reaction evoked discrepancy in views concerning the decomposition reaction mechanism and the role of hydroxyl ion played therein. Pendin and coworkers<sup>1-5</sup> consider hydroxyl ion to be the particle causing the decomposition of ferricenium ion, ferrocene being formed in a subsequent reaction of the non-decomposed ferricenium ions with the products of the primary decomposition, whereas Aly<sup>6,7</sup> ascribes the reduction properties directly to hydroxyl ion.

This communication presents the results of our study of decomposition of ferricenium ion showing the influence of the "inert" salts present in the system and that of the composition of the compounds on the reaction.

## EXPERIMENTAL

### Reagents and Apparatus

Ferricenium perchlorate and tetrafluoroborate were prepared according to Nesmejanov<sup>8</sup> and Allenberg<sup>9</sup>, the compound  $\text{Fe}(\text{C}_5\text{H}_5)_2 \cdot \text{HAlCl}_4$  was prepared according to Pavlík and Šubrt<sup>10</sup>. Solutions of all the reagents were prepared from the water twice redistilled in stream of argon. Before each measurement the same inert gas was bubbled through the solutions for one hour.

The arrangement described by Pendin and coworkers<sup>5</sup> was used for the kinetic measurements. The potential between the ferrocene and the saturated calomel electrodes was measured directly by a digital voltameter NR-20 (Metra, Blansko). pH of the solutions was measured with an OP-201/2 pH-meter (Radelkis, Budapest) using a glass and a saturated calomel electrodes. Stability

constants of the complexes of ferricenium with anions of inorganic salts were determined by the method developed by Pendin and coworkers<sup>11,12</sup>. The spectrophotometry was carried out with a Specord UV VIS apparatus (Zeiss, Jena). All the measurements were carried out under pure argon at  $25 \pm 0.1^\circ\text{C}$ .

#### Analytical Methods

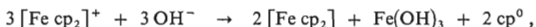
Content of ferricenium ions was determined spectrophotometrically ( $\epsilon_{618\text{nm}} = 430 \text{ l mol}^{-1} \cdot \text{cm}^{-1}$ ) and checked according to Renger and Jeník<sup>13</sup>. Content of the ferrocene precipitated after complete decomposition of ferricenium was determined according to Wolf and coworkers<sup>14</sup>.

### RESULTS

Solutions of  $10^{-3}$  to  $10^{-2} \text{ M}$  ferricenium perchlorate and tetrafluoroborate in oxygen-free redistilled water as well as those in contact with air oxygen become turbid with the precipitated ferrocene within several hours. The same solutions containing equivalent amount of perchloric acid precipitated slight amounts of ferrocene within the first several minutes ( $\sim 4\%$  and  $6\%$  in the case of the perchlorate and tetrafluoroborate, respectively), and then in the course of further eight to ten hours no changes were observed in them. Acid solutions of the ferricenium compounds containing, in addition,  $0.08$  to  $1.00 \text{ M}$  inorganic salts ( $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KNO}_3$ ,  $\text{NaClO}_4$  and  $\text{Na}_2\text{SO}_4$ ) are stable, too. The only observable change was an immediate decrease of potential of the ferrocene electrode after addition of the salts due to formation of the complexes  $[\text{Fe cp}_2 \text{ X}]^{(n-1)-}$ , where  $\text{X}^{n-} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{cp} = \text{C}_5\text{H}_5^-$ . Addition of sodium hydroxide in amounts corresponding to three to twenty-five multiple of the ferricenium amount in the solution produced a rapid change making the solutions to lose gradually their original blue colour and separate ferrocene and iron(III) hydroxide. The attempts to prepare  $\text{Fe}(\text{C}_5\text{H}_5)_2 \cdot \text{HAlCl}_4$  solutions in water or dilute perchloric acid or sodium hydroxide under the above mentioned conditions failed. The dissolution process is accompanied by rapid decomposition resulting in precipitation of  $92$  to  $95\%$  ferrocene. On the basis of this experience we worked with stock solutions containing about  $5 \cdot 10^{-3}$  to  $1 \cdot 10^{-2} \text{ mol l}^{-1}$  ferricenium perchlorate and the same amount of perchloric acid, the ferrocene precipitated on dissolution being removed by filtration. Immediately before the measurements concentration of the stock solutions was additionally adjusted.

*Stoichiometry of reaction of ferricenium ion with  $\text{OH}^-$  ion.* Acid solutions of  $1 \cdot 10^{-3} \text{ M}$  ferricenium perchlorate containing anions of inorganic salts ( $0.08$  to  $1.00 \text{ M}$ ) were treated with sodium hydroxide solution whose amount corresponded (after subtraction of the consumption corresponding to neutralization of free perchloric acid according to pH check) to three to twenty-five multiple of the ferricenium ion content. After complete removal of the ferricenium cation from the solution the ferrocene content was determined. Its amount varied within  $58.2$  to  $67.3\%$  of the original

ferricenium content. The mean value obtained from 54 analyses is 63.4% which is close to two thirds of the original amount of ferricenium ion. Differences between the individual analyses are purely statistical, we could not find any dependence between concentrations of ferricenium ions, perchloric acid, sodium hydroxide, and inorganic salts. Differences in determination of the separated ferrocene in oxygen-free water and non-pretreated water never exceeded the above mentioned limit. Therefore, under the conditions used in our experiments no significance is ascribed to small amounts of oxygen in the reaction mixture. Thus the decomposition of ferricenium ion follows the stoichiometric equation



where  $\text{cp}^0$  means an one-electron oxidation product of  $\text{cp}^-$ .

Results of the reaction of  $\text{Fe}(\text{C}_5\text{H}_5)_2 \cdot \text{HAlCl}_4$  with water and sodium hydroxide suggest that the following neutralization takes place



Kinetics of the decomposition reaction of ferricenium ions by  $\text{OH}^-$  ions were studied in solutions containing excess of both hydroxyl ions and ions of inorganic salts in all the cases. Composition of the solutions was the same as that given in the above paragraph. Under these experimental conditions all the studied systems showed precisely linear time dependence of the ferrocene electrode potential, which corresponds to monomolecular course of the decomposition reaction<sup>1</sup>. Thus the rate of ferricenium ion concentration decrease only depends on their activities under the individual experimental conditions.

$$-d\{[\text{Fe cp}_2]^+\}/dt = k_n\{[\text{Fe cp}_2]^+\}. \quad (1)$$

The constant  $k_n$  is the rate constant of the pseudomonomolecular reaction. Its value increases with increasing  $\text{OH}^-$  ion concentration and decreases with increasing  $\text{X}^{n-}$  ion concentration. Evaluating the dependence  $k_n$  vs  $\text{X}^{n-}$ , we found that influence of the anions  $\text{X}^{n-}$  is not restricted to primary salt effect only (as it is stated by Pendin<sup>3</sup>). Besides that formation of the non-dissociated complexes  $[\text{Fe cp}_2 \text{X}]^{(n-1)-}$  plays an important role. In all further considerations actual activities of particles are used instead of concentrations, so that influence of the primary salt effect might be suppressed. Values of the activities were calculated with the use of the mean activity coefficients given in Tables<sup>15,16</sup>.

The dependence  $k_n$  vs  $\text{OH}^-$  activity is given in Fig. 1. From the course of the dependence it follows

$$k_n = k_{\text{OH}}\{\text{OH}^-\}. \quad (2)$$

Hence, at constant activity of  $X^{n-}$  ion the decomposition of ferricenium ions follows the second order kinetics, being first order in ferricenium ion activity and first order in  $OH^-$  activity, with the rate constant  $k_{OH}$ .

Dependence of  $k_{OH}$  (which equals the measured constant  $k_n$  divided by hydroxyl ion activity) on activity of anions of inorganic salts is given in Fig. 2. The linear character of the functional dependence  $1/k_{OH}$  vs  $\{X^{n-}\}$  corresponds to Eq. (3)

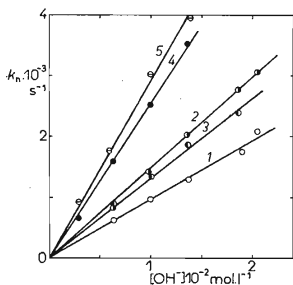
$$k_{OH} = k_{OH}^0 / (1 + k_x \{X^{n-}\}), \quad (3)$$

where  $k_{OH}^0$  is reciprocal value of intercepts at the axis of ordinates of the functional dependences in Fig. 2, and it represents the  $k_{OH}$  constant at zero activity of salts,  $k_x$  is a product of slope of the same functional dependences and the constant  $k_{OH}^0$ , and it represents the decrease of the decomposition rate of ferricenium ion by hydroxyl anion in salt medium of the activity  $\{X^{n-}\}$ .

Combination of Eqs (1) to (3) gives the expression of the decomposition rate of ferricenium ion by action of  $OH^-$  ion in the presence of  $X^{n-}$  ions

$$-d\{[Fe cp_2]^+\}/dt = k_{OH}^0 \{[Fe cp_2]^+\} \{OH^-\} / (1 + k_x \{X^{n-}\}). \quad (4)$$

The  $k_x$  constants were obtained by statistical treatment of the experimental data in Figs 1 and 2 and are given in Table I. The  $k_{OH}^0$  constant, which is independent on



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Dependence of Rate Constant  $k_n$  on Activity of Hydroxyl Ion

1 0.8M-KCl, 2 0.8M-KBr, 3 0.8M-KNO<sub>3</sub>,  
4 0.8M-NaClO<sub>4</sub>, 5 0.4M-Na<sub>2</sub>SO<sub>4</sub>.

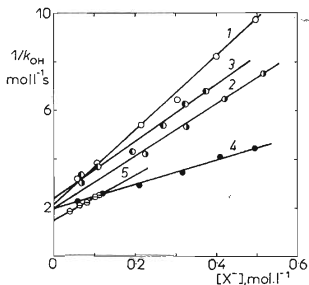


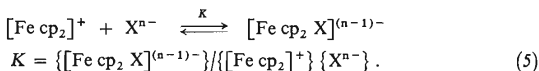
FIG. 2

Dependence of Reciprocal  $k_{OH}$  on Activity of Anions of Inorganic Salts

For numbers see Fig. 1.

activity of salts, gives the average value  $0.51 \pm 0.12 \text{ l mol}^{-1} \text{ s}^{-1}$  for five studied systems with various  $X^{n-}$  anions.

The abovementioned method was used for determination of stability constants  $K$  of the complexes formed by the equilibrium



The  $K$  values of the systems studied by us are summarized in Table I. The equilibrium constants are independent of acidity of the medium. Values of the constants for the complex compounds  $[\text{Fe cp}_2 \text{ Cl}]$  and  $[\text{Fe cp}_2 \text{ ClO}_4]$  agree very well with the literature data<sup>11,17,18</sup>, the other constants have not yet been published.

## DISCUSSION

In our opinion, differences in determination of stoichiometric relations of reaction of ferricenium ion and hydroxyl ion are affected significantly by type and purity of the starting ferricenium compounds. From ref.<sup>19</sup> it is known that the both types  $[\text{Fe cp}_2 X]$  and  $[\text{Fe cp}_2 \cdot \text{HX}]$  are available. The two types differ but little in their preparation, and the both compounds give blue solutions in acid media with characteristic absorption band ( $\lambda_{\text{max}}$  about 615 to 620 nm). It is very likely that the compounds used in the studies of Aly<sup>6,7</sup> are of the second type, and consequently his results correspond with those of our study of reaction of the compound  $[\text{Fe cp}_2 \cdot \text{HAlCl}_4]$  with  $\text{OH}^-$  ions. However, rather unexpected results were obtained by Pendin<sup>5</sup> for the same reaction with ferricenium perchlorate. High ferrocene content (up to 98%) cannot be ascribed (in our opinion) unambiguously to as much as twenty-six electron reduction capacity of cyclopentadienide ion. We do not exclude a more-electron reduction capacity of cyclopentadienide ions. We observed it, too, in oxidations of substituted ferrocene derivatives<sup>20</sup>. However, it made itself felt only in long-lasting (several hours) reactions with strong oxidizing agents as *e.g.*  $\text{Ce}^{4+}$  in strongly

TABLE I

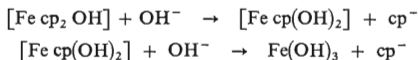
Values of  $k_x$  and  $K$  Constants for Various Anions  $X^{n-}$

Anion	$\text{Cl}^-$	$\text{Br}^-$	$\text{NO}_3^-$	$\text{ClO}_4^-$	$\text{SO}_4^{2-}$
$k_x, \text{ l mol}^{-1}$	$2.5 \pm 0.4$	$4.8 \pm 0.5$	$4.6 \pm 0.7$	$7.2 \pm 0.7$	$6.1 \pm 0.5$
$K, \text{ l mol}^{-1}$	$2.2 \pm 0.4$	$4.0 \pm 0.4$	$4.4 \pm 0.4$	$5.6 \pm 0.5$	$4.5 \pm 0.4$

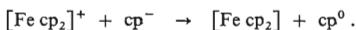
acidic medium. With respect to ferricenium ions cyclopentadienide anion acted as one-electron reducing agent in all the processes studied by us. We consider the explanation to be more acceptable, that Pendin<sup>5</sup> used  $[\text{Fe cp}_2 \cdot \text{HClO}_4]$  or a perchlorate considerably contaminated with this compound. However, from the cited work it is impossible to find composition of the compound.

Decomposition of ferricenium ion by action of hydroxyl ions in aqueous solutions of inorganic salts proceeds in the following way (in our opinion):

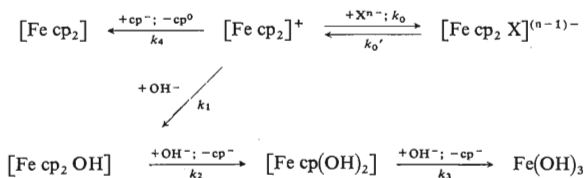
1) Rapid, practically instant equilibrium (Eq. (5)) is established between ferricenium ion and anions of salts. 2) Free ferricenium ions (their activity is given by the stability constant of this equilibrium) are attacked by  $\text{OH}^-$  ion to give the transient complex  $[\text{Fe cp}_2 \text{ OH}]$ . It is possible that in fact a water molecule is replaced by an  $\text{OH}^-$  ion, since ferricenium ion in aqueous solutions is present as dihydrate according to Smith<sup>21</sup>. 3) The unstable intermediate  $[\text{Fe cp}_2 \text{ OH}]$  is rapidly decomposed with gradual liberation of cyclopentadienide ions which are substituted by  $\text{OH}^-$  ions.



4) The cyclopentadienide ions formed by destruction of the sandwich complex  $[\text{Fe cp}_2 \text{ OH}]$  and the monosandwich complex  $[\text{Fe cp}(\text{OH})_2]$  react very rapidly with the yet undecomposed ferricenium ions, so that they compete with the ions  $\text{OH}^-$  in the reactions. The  $\text{cp}^-$  ions act exclusively (or almost so) as one-electron reducing agents under the experimental conditions.



The reaction course is represented by the scheme:



The following formal kinetic relations follow from the scheme:

$$\begin{aligned} -d\{[\text{Fe cp}_2]^+\}/dt &= k_0\{[\text{Fe cp}_2]^+\}\{\text{X}^{n-}\} - k_0'\{[\text{Fe cp}_2 \text{ X}]^{(n-1)-}\} + \\ &+ k_1\{[\text{Fe cp}_2]^+\}\{\text{OH}^-\} + k_4\{[\text{Fe cp}_2]^+\}\{\text{cp}^-\}, \end{aligned} \quad (6)$$

$$d\{[\text{Fe cp}_2 \text{X}]^{(n-1)-}\}/dt = k_0\{[\text{Fe cp}_2]^+\} \{\text{X}^{n-}\} - k'_0\{[\text{Fe cp}_2 \text{X}]^{(n-1)-}\}, \quad (7)$$

$$d\{[\text{Fe cp}_2 \text{OH}]\}/dt = k_1\{[\text{Fe cp}_2]^+\} \{\text{OH}^-\} - k_2\{[\text{Fe cp}_2 \text{OH}]\} \{\text{OH}^-\}, \quad (8)$$

$$d\{[\text{Fe cp}(\text{OH})_2]\}/dt = k_2\{[\text{Fe cp}_2 \text{OH}]\} \{\text{OH}^-\} - k_3\{[\text{Fe cp}(\text{OH})_2]\} \{\text{OH}^-\}, \quad (9)$$

$$d\{\text{Fe}(\text{OH})_3\}/dt = k_3\{[\text{Fe cp}(\text{OH})_2]\} \{\text{OH}^-\}, \quad (10)$$

$$d\{[\text{Fe cp}_2]\}/dt = k_4\{[\text{Fe cp}_2]^+\} \{\text{cp}^-\}, \quad (11)$$

$$d\{\text{cp}^-\}/dt = k_2\{[\text{Fe cp}_2 \text{OH}]\} \{\text{OH}^-\} + k_3\{[\text{Fe cp}(\text{OH})_2]\} \{\text{OH}^-\} - k_4\{[\text{Fe cp}_2]^+\} \{\text{cp}^-\}, \quad (12)$$

$$d\{\text{cp}_0\}/dt = k_4\{[\text{Fe cp}_2]^+\} \{\text{cp}^-\}. \quad (13)$$

This system of equations can be simplified on the basis of the following physical and chemical pieces of knowledge: *a*) The equilibrium (5) is established practically immediately, so that actual activity of ferricenium ion in all reactions of the given scheme is only bound by the equilibrium condition

$$\{[\text{Fe cp}_2]^+\}_r = \{[\text{Fe cp}_2]^+\}_0 / (1 + K\{\text{X}^{n-}\}_r), \quad (14)$$

where the symbols *r* and 0 denote the equilibrium and analytical activities, respectively. The *K* constant means the equilibrium stability constant (Eq. (5)), being equal to  $k_0/k'_0$ . For a large excess of  $\text{X}^{n-}$  ions it is  $\{\text{X}^{n-}\}_r = \{\text{X}^{n-}\}_0$ . In all the other equations activity of ferricenium ion must be considered the equilibrium activity, *i.e.*  $\{[\text{Fe cp}_2]^+\} = \{[\text{Fe cp}_2]^+\}_r$ , whereby the terms containing  $k_0$  and  $k'_0$  are eliminated from Eq. (6). *b*) The reaction is controlled by nucleophilic attack of ferricenium ion and formation of the transient adduct  $[\text{Fe cp}_2 \text{OH}]$ . Therefore, the constants  $k_2$ ,  $k_3$ ,  $k_4$  are much larger than  $k_1$ . This fact is discussed in detail in our previous reports<sup>20,22</sup>. Hence, in the reaction mixture the particles  $[\text{Fe cp}_2 \text{OH}]$ ,  $[\text{Fe cp}(\text{OH})_2]$  and  $\text{cp}^-$  are not accumulated, so that the steady state treatment can be applied to the equations (8), (9) and (12). If they are put equal to zero, it follows that

$$\begin{aligned} k_1\{[\text{Fe cp}_2]^+\} \{\text{OH}^-\} &= k_2\{[\text{Fe cp}_2 \text{OH}]\} \{\text{OH}^-\} = \\ &= k_3\{[\text{Fe cp}(\text{OH})_2]\} \{\text{OH}^-\} = \frac{1}{2}k_4\{[\text{Fe cp}_2]^+\} \{\text{cp}^-\}. \end{aligned} \quad (15)$$

Introduction of the modified expressions from Eqs (14) and (15) in the original system of equations gives relations in which there is only one rate constant ( $k_1$ ) and stability constant (*K*).

$$-d\{[\text{Fe cp}_2]^+\}/dt = 3k_1\{[\text{Fe cp}_2]^+\} \{\text{OH}^-\}/(1 + K\{\text{X}^{n-}\}), \quad (16)$$

$$-d\{[\text{Fe cp}_2 \text{X}]\}/dt = 3k_1K\{\text{X}^{n-}\} \{[\text{Fe cp}_2]^+\} \{\text{OH}^-\}/(1 + K\{\text{X}^{n-}\}), \quad (17)$$

$$d\{[\text{Fe cp}_2\text{OH}]\}/dt = d\{[\text{Fe cp}(\text{OH})_2]\}/dt = d\{\text{cp}^-\}/dt = 0, \quad (18)$$

$$d\{\text{Fe}(\text{OH})_3\}/dt = k_1\{[\text{Fe cp}_2]^+\} \{\text{OH}^-\}, \quad (19)$$

$$d\{[\text{Fe cp}_2]\}/dt = d\{\text{cp}_0\}/dt = 2k_1\{[\text{Fe cp}_2]^+\} \{\text{OH}^-\}. \quad (20)$$

There is formal analogy between Eqs (16) and (4). This bare fact suggests high probability of the proposed mechanism. From comparison of the both equations it follows that the experimental constant  $k_0^{\text{OH}}$  from Eq. (4) corresponds to  $3k_1$  (Eq. (16)). From the proposed mechanism it follows that the  $k_1$  constant corresponds to the rate of nucleophilic attack of ferricenium ion by  $\text{OH}^-$  ion, and, hence, it is independent of activity of the salt anions. In Experimental it has been already stated that this requirement is fulfilled within experimental error. Hence, the  $k_1$  values are about  $0.17 \text{ l mol}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ . The equilibrium constant  $K$  from Eq. (14) is a counterpart of the  $k_x$  constant from Eq. (4). Very close values of the both constants confirm reliability of the proposed mechanism. In no case the influence of oxygen in decomposition reactions of ferricenium ions is to be underestimated. However, under the experimental conditions used its reactivity to all the reaction components is relatively low, so that the reactions described above predominate for kinetic reasons.

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